

DRAWINGS ATTACHED.

1,023,471



*Date of Application and filing Complete Specification:*  
Oct. 15, 1962. No. 38945/62

*Application made in United States of America (No. 145,238) on*  
Oct. 16, 1961.

*Complete Specification Published: March 23, 1966.*

© Crown Copyright 1966.

Index at Acceptance:—D1 P(A1, B2A1, B2A2, B2B1, B2B2, B2BX, B5A, B5B, B5C, C1H1B, C1H1X, C1J, C2A10, C2A11, C2A12B4, C2C5, C2C7, C2C8, C2C9, C2C10, C2C11, C2C16, C2C18); D1 L23D.

Int. Cl.:—D 06 m /D 06 b.

## COMPLETE SPECIFICATION.

## Process for Treating Cellulosic Fabric and Product thereof.

We, DEERING MILLIKEN RESEARCH CORPORATION, a corporation organized under the laws of the State of Delaware, United States of America, of P.O. Box 1927, Spartanburg, South Carolina, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a novel process for the treatment of cellulosic fabrics, more particularly to a method of applying limited amounts of moisture and strong base as part of a process for wet cross-linking of cellulosic fabrics and fabrics thus produced.

It has been found that base catalyzed wet cross-linking reactions, i.e., cross-linking reactions catalyzed with strong base in which the cross-linking of the cellulosic molecules is conducted in the presence of strong base and moisture, which heretofore were believed to impart only wet resiliency to fabric, i.e., flat drying properties after wringing out by hand or passing through the spin cycle of an automatic washer and line drying, can impart good dry resiliency to the fabric, i.e., flat drying properties when dried in an automatic tumble dryer, if the reaction is conducted in the presence of relatively small amounts of moisture. One means of achieving this is to apply a dilute aqueous solution of the selected strong base to the fabric by conventional means, e.g., by a padding operation, and then drying the fabric to the desired moisture content before applying the cross-linking agent. Such a procedure is not always desirable in production because it requires costly drying equipment with sensitive controls and also because the fabric is

susceptible to damage due to over-drying in the drying operation, e.g., during the frequent stoppages that occur in a production run.

To avoid this drying operation, it is theoretically possible to apply limited amounts of strong base in the form of a concentrated aqueous solution by means of an applicator roll, spray or knife coating. However, when such expediences are attempted, the inevitable consequence is that the fabric puckers because the concentrated strong base solution is not applied uniformly. In the case of applicator rolls, continuous lateral and longitudinal transfer of thin films of the catalyst solution from the applicator roll to the fabric is impossible to achieve. Also, surface tension and other forces cause the film to break as the applicator roll contacts the fabric, thereby causing the portions of the fabric that are wet first to attract further amounts of the solution at the expense of neighboring areas. Similar problems are associated with knife coating and spraying because there is little restraint on the fabric in the form of tension or pressure as the strong base solution strikes the fabric.

That the fabric puckers is not surprising, in view of the fact that the uneven application of strong aqueous solutions of sodium hydroxide is the standard technique for obtaining the three dimensional plisse-type fabrics. Thus, while it appeared theoretically possible to achieve the desired cross-linking reaction in the presence of limited amounts of moisture by employing applicator roll or spray techniques to apply small amounts of concentrated aqueous solutions of the strong base catalyst, the puckering associated with this procedure makes the

[Pric

technique of applying an excess of moisture, in the form of a more dilute strong base solution, and thereafter drying the fabric to the desired moisture content appear to be commercially a necessary procedure for uniformly distributing strong base in a fabric and yet also provide a low moisture content therein.

It has now been found that the puckering heretofore believed to be inevitable when concentrated aqueous solutions of strong base are applied to a fabric can be avoided when following the process of this invention.

It is therefore an object of this invention to provide a novel process for applying limited amounts of a concentrated aqueous solution of strong base to cellulosic fabrics in a wet cross-linking process to produce wet resiliency and without producing puckering therein.

It is another object to provide a process for wet cross-linking fabric in the presence of strong base involving the application of an aqueous solution of a strong base to the fabric which process obviates the necessity of a drying step.

A further object is to provide a novel process for producing cellulosic fabric having good wet and dry resiliency without heating the fabric as a step of the process.

According to this invention the hydroxy groups of a cellulosic fabric are cross-linked with a strong base catalysed cross-linking agent while the fabric contains a strong base as herein defined and less than 35% by weight total moisture, an aqueous strong base solution being uniformly applied to the cellulosic fabric by transfer of the solution with pressure from a printroll having a pattern on the surface thereof in an amount such that the total moisture content of the fabric does not exceed 35% by weight, to impart good dry resiliency as well as wet resiliency to the fabric. The cross-linking agent may be applied to the fabric either before or after application of the strong base.

The invention also comprises cross-linked cellulosic fabric characterised by a uniform pattern of cross-linking detectable by dyes receptive to cross-linked cellulose, but relatively unreceptive to uncross-linked cellulose, the pattern being geometric and having relatively highly cross-linked portions of the fabric separated by portions having a substantially lesser degree of cross linking, said latter portions having an area not greater than 0.05 square inch.

This invention is illustrated by the accompanying drawing, which is a schematic perspective view of an apparatus which can be employed for following the process of this invention.

As illustrated by the drawing substantially dry fabric F, shown in broken lines, is removed from a conventional source of supply,

e.g., a supply roll 1, and passed in intimate contact with the patterned surface 3 of printroll 2, provided by fine lines 4 in the surface thereof. Continuous contact of the fabric F with the textured surface 3 of printroll 2 is ensured by a pressure roll 5 whose axis is parallel to the axis of printroll 2 and positioned so as to provide a nip through which the fabric F passes. The aqueous strong base solution is contained in the reservoir 6 and picked up therefrom by printroll 2. Excess solution is removed by doctor blade 7, so that only the strong base solution which is trapped in the patterned surface 3 is transported to the fabric F. The fabric F then passes over a conventional applicator roll 10 which can apply the cross-linking reagent contained in the reservoir 11 to the fabric F. The fabric F then passes to a conventional take-up means, illustrated by a take-up roll 20, or passed through other conventional fabric processing equipment. In an alternate procedure, not shown in the drawing, the applicator roll 10 and reservoir 11 can be placed intermediate the roll 1 and the printroll 2 so that the cross-linking agent or an organic solution thereof can be applied first. If the starting fabric F already has uniformly impregnated therein the selected cross-linking agent, then applicator roll 10 and reservoir 11 can be omitted.

Cellulosic fabrics which are cross-linked according to the process of this invention are those formed of materials which are normally cross-linked to impart wet configurational memory thereto, e.g., natural and regenerated cellulose including those having a portion of the free hydroxy groups esterified or etherified, i.e., so that at least 1.8 free hydroxy groups per anhydroglucose unit remain, e.g., lower-hydrocarbon esters including the acetate, propionate, butyrate, amyl esters such as the benzoate and inorganic esters such as the sulfate, phosphate, aryl and alkyl sulfate esters, lower-alkyl ethers including methyl and ethyl ethers and hydroxyalkyl ethers including hydroxyethyl ethers and carboxymethyl ethers. Fabrics can consist of natural cellulosic materials, e.g., cotton, linen, jute or flax or the synthetic cellulosic materials, e.g., filament or staple viscose rayon, both unmodified and modified, e.g., the polynosic rayons. The novel process is directed primarily and preferably to woven cellulosic textile fabrics, but the advantages of this invention can also be achieved by treating non-woven or knitted fabrics. The preferred cellulosic material is cotton which is preferably woven, e.g., printcloth, broadcloth and sheeting. Although the process will ordinarily be conducted on fabric consisting entirely of cotton or viscose rayon, the process is equally applicable to fabrics comprising synthetic filaments or fibers, e.g., the ethylene glycol-terephthalate

polyester, nylon, and polyacrylics fibres. Preferably the cellulosic material comprises at least 40% or more by weight of the fabric to be treated and more desirably 60% or more. It will be apparent to those skilled in the art to which this invention pertains that because regenerated cellulose and certain of the cellulose derivatives tend to be adversely affected by aqueous alkali-metal hydroxide solutions of high concentration, if these materials are present in the fabrics to be treated, care should be taken that the strong base catalyst does not adversely affect the cellulosic material, e.g., by employing lower concentrations or alkali-metal salts.

The strong base catalysts for the cross-linking reaction include the alkali-metal hydroxides, e.g., sodium hydroxide and potassium hydroxide, the quaternary ammonium hydroxides, e.g., trimethylphenyl ammonium hydroxide, and alkali-metal salts which, in the presence of moisture, produce a strongly alkaline solution, e.g., the alkali-metal sulfides and alkali-metal silicates. When the salts are employed, they should be employed in amount which will impart an alkalinity to the solution in about the same range as that obtained when an alkali-metal hydroxide is employed.

The cross-linking agents employed in the process of this invention are the strong base catalyzed cross-linking agents, including epichlorohydrin, 1,3-dichloropropanol-2, 2,3-dichloropropanol-1, and mixtures thereof, the diglycidyl ethers of glycerol and ethylene glycol and related haloepoxide, dihalohydrin and diepoxide cross-linking agents, e.g., those disclosed in British Patent Specification No. 855,547. Other suitable cross-linking agents are divinyl sulfone, divinyl sulfoxide, and compounds represented by one of the formulae  $(R-O-CH_2CH_2)_2SO_2$  and  $(R-O-CH_2CH_2)_2SO$ , wherein R is the acyl radical of an organic acid, e.g., acetic, propionic or other lower-hydrocarbon carboxylic acid, the acyl radical of a monobasic or polybasic strong acid, e.g., sulfato, phosphato or alkali-metal salts of sulfato or phosphato radicals. Epichlorohydrin is preferred among the alkali catalyzed wet cross-linking agents in the process of this invention for several reasons. First, it neutralizes the strong base catalyst, so that the degree of cross-linking can be controlled by the amount of alkaline catalyst applied to the fabric. Secondly, only one molar equivalent of strong base catalyst is consumed, thereby avoiding the necessity of applying large amounts of alkaline catalyst to the fabric. Also, the volatility of the epichlorohydrin ensures that uniform cross-linking will take place, so long as the strong base catalyst is uniformly distributed on the cellulosic material, even though the epichlorohydrin itself is not absolutely uniformly applied.

The printroll employed in the process of this invention is, of necessity, formed of a material which is inert to aqueous strong base solutions, e.g., chrome plated copper, stainless steel, Teflon or polypropylene ("Teflon" is a Registered Trade Mark). The patterned surface can be provided in the usual fashion, e.g., by photo engraving, knurling, machine threading, or cutting or scratching in any convenient manner. The pattern shown in the drawing is a cross hatched type pattern, but the pattern can take a wide variety of forms, e.g., parallel lines running helically, vertically or horizontally around the roll, or combinations of these intersecting to form a cross-hatched pattern, and can be continuous lines, intermittent lines, dots or bands of lines or dots on the surface. Parallel horizontal or substantially horizontal continuous or intermittent lines or dots or bands of lines or dots 0.01 to 0.1 inch apart are preferred when the fabric is passed over the printroll warpwise and it is desired to retain maximum strength in the fabric fillingwise. While it will be apparent that the pattern can be obtained by providing raised portions on the surface of the roll, a more convenient expediency is to etch or groove the surface of the roll. The depth and width of the etched or grooved portions can be varied to control the pick-up of the strong base solution. For example, the depth can be varied from 0.0005 inch or less to 0.005 inch or more, the width can be from that of a single line to an etched band 0.05 to 0.2 inch or more wide and the smooth or unetched portions can be the distance between thread lines of from 4 to 20 or more per inch or strips 0.0005 to 0.2 inch or more wide between etched bands. The unetched portions, i.e., the portions which do not transfer any substantial amount of strong base catalyst to the fabric preferably have a width no greater than 0.1 inch or more preferably no greater than 0.05 inch. Thus, when these portions are square, as shown in the drawing, they preferably have an area no greater than 0.05 square inch.

It will be apparent from the description of the printroll that the term "uniformly" as used herein does not mean that the strong base catalyst and/or moisture is absolutely uniformly applied as is obtained when fabric is padded through an aqueous solution and then squeezed to the desired pick-up. Rather, the term "uniformly" means that relatively large areas, e.g., 0.1 to 1 sq. inch, of fabric will have substantially the same moisture and strong base content as other relatively large areas. On the other hand, the patterned surface of the printroll produces minute irregularities in moisture and strong base content in very small areas of the fabric and, in fact, it is this "patterned uniformity" which appears to produce the desirable and

novel results obtained according to this process. One manifestation of this novel effect is good dry resiliency can be produced in fabric containing up to 35% by weight total moisture, whereas if the fabric is impregnated, e.g., by padding, with a large volume of strong base solution and then dried to a lower moisture content, the total moisture content of the fabric must be below 15% by weight before substantial dry resiliency is imparted to the fabric. This may be due to the fact that because the strong base is applied at fairly high concentrations, the high strong base concentration may tend to counter act the adverse effect on dry resiliency produced by higher moisture levels. In any event, it is quite apparent that the adverse effects of moisture in producing dry resiliency in the cross-linked fabric are manifested at a higher moisture level when following the process of this invention than when attempting to impart dry resiliency by drying the fabric after applying large volumes of aqueous strong base solutions.

If the pattern on the printroll is relatively coarse, the fabric will be cross-linked in a pattern which can be rendered visible by dyeing the fabric with dyes which have a greater affinity for the cross-linked portions than for the portions relatively free from cross-linking, e.g., Celleton Blue FFRS. This technique is desirable for obtaining patterned dyeing effect in a bath dyeing procedure.

Another novel effect which can be obtained with the process of this invention, particularly with heavier fabrics and for low catalyst solution pick-ups and higher concentrations thereof, e.g., above 10—15% by weight and preferably above 15—20% concentration, e.g., 25%—50%, with pick-ups below 25% by weight and preferably below 10—15%, e.g., as low as 2—5%, is that "single face" cross-linking can be obtained, i.e., one face of the fabric can be cross-linked while the opposite face is obtained relatively free from cross-linking. This has the advantage of providing fabric with good wet and dry resiliency while retaining a higher percentage of its starting strength and/or abrasion resistance.

In carrying out the process of this invention, the desired wet cross-linking reaction to impart wet and dry resiliency to the fabric is conducted under conditions whereby an aqueous solution of the selected strong base catalyst is applied to substantially dry fabric by means of the above-described printroll with pressure under conditions of pick-up so that the fabric containing the strong base catalyst also contains less than 35% by weight total moisture. "Substantially dry" fabric means that the fabric contains about the moisture which is present in conditioned fabric, e.g., from 1% to 14%, the exact

moisture ordinarily being dependent upon the relative humidity of the atmosphere in which the starting fabric was stored. The amount of cross-linking agent which is applied to the fabric will depend, in part, upon the degree of wet and dry resiliency desired to be imparted to the fabric and on the selected cross-linking agent. For example, if the cross-linking agent does not consume the strong base catalyst, then only that amount of cross-linking agent which will produce the desired degree of cross-linking should be applied to the fabric. In the case of epichlorohydrin and compounds which consume a molar equivalent of the strong base catalyst, it is ordinarily preferred to employ a molar equivalent or more of the cross-linking agent and control the degree of cross-linking by the amount of strong base catalyst applied to the fabric. If the cross-linking agent consumes two molar equivalents of strong base catalyst, it is ordinarily preferred to apply a half a molar equivalent or less of the cross-linking agent. With the cross-linking agents which consume a molar equivalent of the strong base catalyst, the usual amount of strong base catalyst which is applied to the fabric is between 0.5% and 6%, preferably 1%—5%, and more preferably 2%—4%, calculated on the weight of the dry fabric. Between 0.25% and 2% by weight is ordinarily applied with cross-linking agents which do not consume the strong base catalyst and between 2% and 15% by weight is applied when the cross-linking agent consumes two molar equivalents of strong base catalyst.

By the term "strong base" as used herein is meant a substance which is soluble in water and, as a 1% by weight aqueous solution, has a pH of at least 10.

The aqueous strong base solution can be applied before, concomitantly with or after the cross-linking agent. It is possible to provide emulsions of the selected cross-linking agent, strong base and water so that the appropriate amounts of moisture, strong base and cross-linking agent are applied simultaneously to the cellulosic material. However, such emulsions are stable for only a short period of time and it is thus ordinarily preferred to apply the cross-linking agent separately from the water and strong base or at least separately from the strong base. If the selected cross-linking agent is non-volatile, it can be applied to the fabric in a prior padding operation and the solvent therefor, either aqueous or organic, then removed by heating the fabric. Also, the cross-linking agent can be applied per se or as a solution thereof by means of an applicator roll or other suitable means before the fabric is passed into contact with the printroll. However, it is ordinarily preferred to apply the cross-linking agent after the aqueous

strong base has been distributed on the fabric by the printroll.

The amount of catalyst solution which is transported to the fabric by the printroll can be regulated, in part, by employing a doctor blade which functions in the usual manner, i.e., to remove the catalyst solution from the smooth, unetched portions while leaving a thin film of the solution on the recessed or etched portions. The rigidity of the doctor blade, the angle it makes relative to the tangential plane of the printroll and the point of contact and the pressure applied by it to the printroll can be used to vary the amount of catalyst solution transported to the fabric. If the pattern of the printroll is essentially horizontal, then the doctor blade is preferably slashed or skewed relative to the axis of the printroll while still maintaining continuous transverse contact with the printroll along its length.

The strong base catalyst which has been uniformly distributed on the patterned surface of the printroll is then transferred therefrom to the fabric with the aid of pressure, normally provided by a pressure roll companion to the printroll. The amount of pressure is not critical so long as the fabric is continuously and firmly in contact with the printroll along its entire width. However, some pressure is necessary as insufficient or no pressure results in spotty and streaked transfer of the catalyst solution which, in turn, results in non-uniform cross-linking results. Generally, a pressure of as little as 0.5 lb./sq. in. is all that is required although higher pressures in the order of 1—10 lbs./sq. in. or higher are ordinarily desired and preferred. Desirably, the pressure roll has associated adjusting means for regulating the amount of pressure. In this way, the transfer of catalyst solution from the printroll to the fabric can be adjusted, e.g., from 50%—100% by weight. The pressure roll is ordinarily formed of a resilient material, e.g., silicone rubber, so that the fabric can be brought into intimate contact with the pattern of the printroll. If the printroll is formed of a resilient material, then ordinarily the pressure roll is formed of a non-resilient material, e.g., stainless steel.

The optimum amount of total moisture below the 35% by weight range which should be present in the fabric during the cross-linking reaction will depend, in part, on the amount of strong base catalyst employed. As stated above, the technique employed in this invention for applying the strong base to the fabric appears to provide more efficient reaction conditions so that substantial dry resiliency can be obtained at moisture levels which will not produce substantial dry resiliency when this catalyst is applied by padding the fabric through the solution and removing a portion of the moisture by drying

the fabric. Generally, it is preferred to maintain a total moisture content below 25% and more preferably between 10% and 20%. To obtain total moisture content below 6—8%, it is ordinarily necessary to dry the fabric in an oven before applying the catalyst solution. As the total moisture content of the fabric falls below 10—15%, the efficiency of the reaction improves considerably and as little as 0.5—1.5% alkali-metal hydroxide need be present in the fabric to achieve substantial dry resiliency in the fabric, whereas by ordinary procedures of applying the strong base catalyst even good wet resiliency is not obtained at these low catalyst levels. Optimum performance-strength loss ratios appear to occur when catalyst solutions of a concentration between 5% and 50%, preferably between 10% and 30% and more preferably between 15% and 25% are employed.

If desired, the fabric can have impregnated in it during the cross-linking reaction, softeners, e.g., of the dispersible polyethylene type, to improve tear strength and can also contain hydroxy compounds, in amount preferably between 0.5%—20% and more preferably between 1%—10%, calculated on the weight of the dry fabric, e.g., lower-alkanols, e.g., methanol, ethanol, and propanol, glycols, e.g., ethylene glycol and propylene glycol, glycerine, sucrose, dextrose, sorbitol, dextrans and starch, which compounds tend to reduce the strength loss produced by the cross-linking reaction.

The fabric containing the strong base catalyst, moisture and selected cross-linking agent is preferably maintained at a temperature up to 100°C., more preferably between room temperature and 60°C., until the desired cross-linking reaction has taken place. These temperatures refer to the environmental temperatures in which the cellulosic material is maintained. The actual temperature of the cellulosic material may exceed these temperature ranges due to the exothermic nature of the reaction. It will be appreciated that, if the temperature is above the boiling point of the selected cross-linking agent, in the interest of efficiency, it is desirable to conduct the process in a closed chamber. Ordinarily, it is preferred that the environmental temperature is at least 25°C. so that the cross-linking reaction will proceed at a reasonable rate. When the environmental temperature in which the cellulosic material is maintained as between 60°C. and 100°C., the reaction is substantially complete in from a few seconds to a few minutes. However, it is ordinarily preferred to conduct the reaction while the cellulosic material is in an environmental temperature between 20°C. and 60°C. and with these conditions, particularly if the cellulosic material is in a compacted state, the reaction is substantially complete in less than six hours.

When the desired cross-linking reaction has taken place, the fabric is then ordinarily washed thoroughly to remove any last traces of reactants and by-products and finished in the usual manner, e.g., by drying in a tenter frame. When the preferred reactant and reaction conditions are employed, the resulting cellulosic material thus obtained will have outstanding dry and wet resiliency which means that the fabric can be passed through the spin cycle of an automatic washer and then line or tumble dried and obtained in a relatively wrinkle-free state. Also, the fabric will resist mussing and wrinkling during storage and use. For example, cotton fabric of the broadcloth, sheeting or printcloth type will often rate 4.0 or better by the standard flat drying test after being spin and line dried or spin and tumble dried. Also, the fabric will often retain about 50% or more of its bleached or mercerized strength.

The following examples are illustrative of the products and processes of this invention

but are not to be construed as limiting. The percentage compositions referred to in these examples are by weight.

#### EXAMPLE I

4.0 yds./lb. bleached and mercerized cotton printcloth and 3.19 yds./lb. 40" cotton broadcloth containing 6—8% moisture were passed through apparatus similar to that shown in the drawing in which printroll pattern NaOH concentrations and pick-ups thereof were varied. After the strong base solution was applied to the fabric, the still smooth fabric was immediately passed over an applicator roll which applied 10—15% epichlorohydrin, calculated on the weight of the NaOH impregnated fabric. The fabric was then aged as a polyethylene encased smooth roll at 55°C. overnight. The fabric was then washed and tested. The results of these tests are shown in Table I below. Substantially identical results are obtained when the fabric is maintained at room temperature overnight.

TABLE I

Sample No. and Fabric	Roll Pattern	% NaOH Concentration	Solution	% Pick-up <sup>1</sup> NaOH	H <sub>2</sub> O	Filling Tensile (Lbs.)	Dry <sup>2</sup> Crease Angle	Flat Dry Rating <sup>3</sup> Spin	Tumble
<b>80×80 Cotton Printcloth</b>									
1	f	50	—	1.5	—	45	—	1.0	1.0
2	f	20	3	2.2	1.5	22.3	242	4.3	4.7
3	g	20	11.0	4.4	8.8	22.3	229	5.0	4.5
4	f	20	22.0	2.0	17.6	20.2	230	5.0	4.3
5	g	20	10	4.8	8.0	22.5	242	5.0	4.9
6	f	20	24	2.0	19.2	19.2	228	5.0	4.5
7	g	20	10	3.6	14.4	21.5	243	5.0	4.8
8	a	50	18	1.3	1.3	19.8	241	5.0	4.4
9	c	50	2.6	1.4	1.4	30.8	209	3.5	3.5
10	e	50	2.8	1.1	1.1	22.4	221	3.5	3.5
11	a	40	2.2	6.4	9.6	26.0	229	3.0	3.5
			16.0			21.2	246	4.8	4.8
<b>136×64 Cotton Broadcloth</b>									
12	a	20	—	4.0	—	65	—	1.0	1.0
13	b	20	20.0	5.4	16.0	24.3	249	5.0	4.0
14	c	20	27.0	3.6	21.6	24.4	234	4.7	3.7
15	d	20	18.0	4.5	14.4	24.9	237	5.0	4.2
16	e	20	22.5	3.0	18.0	26.4	234	4.8	3.8
17	a	15	15.0	2.6	12.0	26.0	243	5.0	4.3
18	a	15	17.3	2.6	14.7	29.5	191	5.0	4.3
19	c	15	19.3	2.9	16.4	29.5	191	5.0	4.3
20	d	15	23.3	3.5	19.8	30.4	186	5.0	4.3
21	e	15	14.7	2.2	12.5	28.6	192	5.0	4.0
22	a	10	18.2	1.8	16.4	28.4	189	5.0	4.3
23	b	10	28.0	2.8	25.2	33.4	167	4.2	3.9
24	c	10	20.9	2.1	18.8	31.8	170	4.7	3.9
25	d	10	25.0	2.5	22.5	35.0	172	4.7	3.9
26	e	10	15.0	1.5	13.5	32.4	168	4.7	3.9
						32.4	179	4.0	3.9

TABLE I—*contd.*

- a. very fine check  $1/32" \times 1/32"$  dotted lines (no pattern visible when NaOH contains dye)  
 b. fine diamond  $1/32" \times 1/32"$  lines (prints visible pattern)  
 c. small star  $1/12" \times 1/12"$  lines (prints visible pattern)  
 d. small check  $1/12" \times 1/12"$  dotted (prints visible pattern)  
 e. fine check  $1/10" \times 1/10"$  dotted bands (slight pattern visible)  
 f. very fine cross-hatched (no pattern visible)  
 g. coarse cross-hatched (prints visible pattern)  
 1. Calculated on weight of starting conditioned fabric  
 2. ASTM Designation 1295-53T  
 3. AATCC Test Designation T-88-1958

## EXAMPLE II

The procedure of Example I was followed, employing aqueous potassium hydroxide of various concentrations and at various pick-ups as the cross-linking catalyst. The results of these runs are shown in Table II, below.

TABLE II

Sample No. and Fabric	Roll Pattern	% KOH Concentration	Solution	% Pick-up <sup>1</sup> KOH <sup>4</sup>	H <sub>2</sub> O	Filling Tensile (Lbs.)	Dry <sup>2</sup> Crease Angle	Flat Dry Ratings <sup>3</sup> Spin Tumble
80×80 Cotton Printcloth	—	—	—	—	—	50	—	1.0
1 do	f	27.5	11.5	2.2	8.4	23	190	5.0
2 do	g	do	22.5	4.4	16.3	19.5	198	5.0
3 do	f	do	9.0	1.9	6.3	22.5	176	4.9
4 do	g	do	21.0	4.1	15.2	20.7	191	5.0
5 do	h	35	10.0	2.5	6.5	21.0	223	5.0
6 do	g	do	21.0	5.2	13.6	20.5	202	5.0
7 do	h	do	12.0	3.0	7.8	21.7	219	5.0
								4.2

1. Calculated on weight of starting conditioned fabric
2. ASTM Designation 1295-53T
3. AATCC Test Designation T-88-1958
4. Pick-up calculated as equivalent amount of NaOH



## EXAMPLE III

The procedure of Example I can be employed to cross-link with divinyl sulfone by substituting divinyl sulfone or preferably a 1%—50% solution thereof in, e.g., acetone, tertiary butanol or isopropanol, so as to apply limited amounts thereof, thereby avoiding over-reaction and excessive embrittlement of the fabric, for the epichlorohydrin in the reservoir used in conjunction with the applicator roll.

Similarly 1,3-dichloropropanol-2 or 2,3-dichloropropanol-1 or a solution thereof in a suitable organic solvent, can be substituted for the epichlorohydrin. In this situation, there should be applied to the fabric at least 2 molar equivalents of base catalyst for each mole of dichloropropanol applied.

## EXAMPLE IV

136×64 cotton broadcloth is impregnated uniformly with a 14% solution of bis-(sodium  $\beta$ -sulfatoethyl)sulfoxide with a 60% pick-up by padding and passing through squeeze rolls. The fabric is passed through a drying oven in a tenter frame and dried to a 6%—8% moisture content. The dried fabric is then passed through the nip provided by a stainless steel patterned printroll and a rubber pressure roll, the printroll having a cross-hatched surface whose grooves are 0.001 inch in depth and spaced 10 to the inch in both directions. The printroll is arranged in conjunction with a reservoir containing 18% aqueous NaOH solution so that the printroll transfers the solution to the fabric with substantially all except that retained in the cross-hatch pattern being removed by a doctor blade. The pressure roll and doctor blade pressures are adjusted so that a 17% pick-up of the aqueous NaOH solution is obtained, calculated on the weight of the dried fabric, thus providing a 3% pick-up of NaOH and 14% pick-up of water. The fabric is maintained in smooth roll form for 3 hours and then washed thoroughly. The thus cross-linked fabric has excellent wet and dry resiliency and flat drying properties.

To vary the extent of cross-linking, the concentration of the sulfoxide solution can be varied from 10% to 35%. The NaOH concentration and pick-up thereof should be adjusted so that 2 or more molar equivalents, calculated on the sulfoxide present in the fabric, is applied to the fabric.

Substantially the same results are obtained by substituting bis-(sodium  $\beta$ -sulfatoethyl)sulfone for the sulfoxide compound in the above process. Because of the rapidity of the reaction, a dwell time of only a few minutes or less is required before the fabric is washed to remove reaction by-products and any residual reactants. Similarly, the corresponding bis-thiosulfato, potassium sul-

fato, ammonium sulfato and quaternary ammonium halides, e.g., pyridinium chloride, picolinium chloride, and isoquinolinium compounds, can be used as cross-linking agents according to the same procedure.

## WHAT WE CLAIM IS:—

1. A process for imparting good dry and wet resiliency to a cellulosic fabric comprising cross-linking the hydroxy groups of the cellulosic fabric with a strong base catalysed cross-linking agent while the fabric contains a strong base as hereinbefore defined and less than 35% by weight total moisture, the strong base being uniformly applied to the fabric in the form of an aqueous solution by transfer of the solution with pressure from the patterned surface of a printroll in an amount such that the total moisture content of the fabric does not exceed 35% by weight.
2. A process according to claim 1, wherein the printroll pattern comprises portions recessed to a depth of from 0.0005 to 0.005 inch into the surface of the printroll, which portions are separated by relatively raised portions having a width no greater than 0.1 inch.
3. A process according to claim 2, wherein the relatively raised portions have an area no greater than 0.05 square inch.
4. A process according to any of the preceding claims, wherein the fabric contains less than 25% by weight total moisture during the cross-linking reaction.
5. A process according to any of the preceding claims, wherein the strong base is an alkali metal hydroxide.
6. A process according to claim 5, wherein the aqueous solution of the strong base has a concentration between 5% and 50% by weight.
7. A process according to claim 6, wherein the aqueous solution of the strong base has a concentration between 10 and 30% by weight.
8. A process according to claim 7, wherein the aqueous solution of the strong base has a concentration between 10 and 25% by weight.
9. A process according to any of the preceding claims, wherein the cross-linking agent is one which consumes one molar equivalent of the strong base and the amount of strong base applied to the fabric is between 1% and 5% by weight, calculated on the weight of the dry fabric.
10. A process according to claim 9, wherein the amount of strong base applied to the fabric is between 1% and 4% by weight.
11. A process according to claim 9 or claim 10, wherein the cross-linking agent is epichlorohydrin.
12. A process according to claim 11,

wherein a molar excess of epichlorohydrin is used calculated on the strong base.

13. A process according to any of claims 1—8, wherein the cross-linking agent is one which does not consume the strong base, and the amount of strong base applied to the fabric is between 0.25% and 2% by weight, calculated on the weight of the starting fabric.

14. A process according to any of claims 1—8, wherein the cross-linking agent is one which consumes two molar equivalents of the strong base, and the amount of strong base applied to the fabric is between 2% and 15% by weight, calculated on the weight of the starting fabric.

15. A process according to any of the preceding claims, wherein the fabric is cotton fabric.

16. A process according to claim 15, wherein the cotton fabric is woven.

17. A process according to any of the preceding claims, wherein the cross-linking agent is applied to the fabric after the aqueous solution of the strong base.

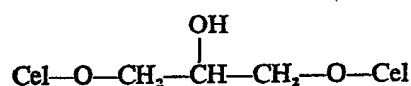
18. A process according to claim 17, wherein, immediately after applying the cross-linking agent, the fabric is rolled into a smooth roll which is maintained until the desired cross-linking reaction has taken place.

19. A process according to claim 1 for imparting good dry and wet resiliency to a cellulosic fabric substantially as hereinbefore described with particular reference to the Examples.

20. Cross-linked cellulosic fabric when produced by the process of any of the preceding claims.

21. Cross-linked cellulosic fabric characterised by a uniform pattern of cross-linking detectable by dyes receptive to cross-linked cellulose, but relatively unreceptive to uncross-linked cellulose, the pattern being geometric and having relatively highly cross-linked portions of the fabric separated by portions having a substantially lesser degree of cross-linking, said latter portions having an area not greater than 0.05 square inch.

22. Cross-linked cellulosic fabric according to claim 21, characterised by a structure of repeating units represented by the formula



For the Applicants,  
GILL, JENNINGS & EVERY,  
Chartered Patent Agents,  
51/52, Chancery Lane, London, W.C.2.

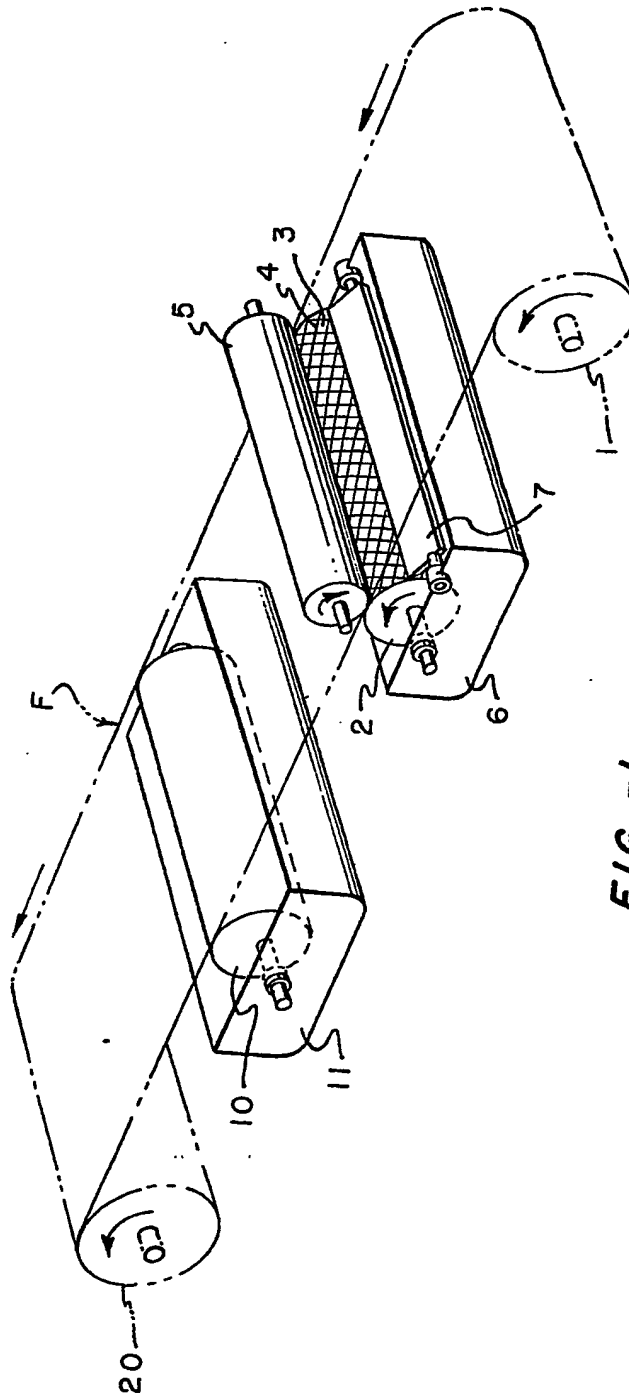


FIG. -1-